Recycling of Lead using Ausmelt Technology

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1 Introduction

The market trends for lead producers may not have been seen as particularly helpful or positive in recent decades, but the patterns are now becoming clear. Supplies are increasingly from secondary sources, especially from spent lead acid batteries. And stringent environmental regulations in many countries are adding to the economic pressures on the secondary lead processors.

Modern smelting technologies can provide economic and environmental benefits to cope with these trends and enable secondary lead processors to exploit market niches. This paper reviews conventional secondary lead processing and Ausmelt Technology for recovery of lead from lead acid batteries, and their performance in complying with environmental regulations.

2 Changing Lead Markets

2.1 Markets for lead and zinc diverge

The patterns of demand and production for lead and zinc have diverged in recent decades, and will continue to grow more distinct in the future. Although they have historically been mined and produced together, these two key industrial metals are progressively being disengaged from dependence on each other. This divergence is being driven by different rates of growth in demand, changing technologies for production and the impact of recycling.

World lead and zinc supplies have grown from an estimated 3.2 and 3.1 million tonnes in 1960, to 6.2 and 8.0 million tonnes respectively in 1999 [1]. This translates to average annual growth rates over this 39-year period were 1.8% and 2.5% respectively.

The production of lead has become a smaller industry than zinc. Lead's share in the Western World's non-ferrous production fell from 8% in 1960 to 4.5% in 1999, while zinc's share grew from 10% to 12% over the same period. These trends in demand are reflected in the relative prices of lead and zinc over this period.

2.2 Factors in lead markets

The decrease in lead production is primarily due to reduced consumption because of increasing awareness of lead's toxicity and other impacts on human health and the environment. The use of lead in many products has been banned or superseded by other, less harmful components, such as titanium dioxide as an opacifier and pigment in paints.

The end-uses for lead have changed over the past four decades with the majority of the world's lead production currently being used for lead acid batteries, as shown in Table 1:

Table 1: Change in Lead Market Segments, 1960 - 2000

%	1960	2000
Lead-acid batteries	30	75
Rolled products	39	8
Chemicals, alloys, etc	31	17
Total	100	100

Consumption patterns vary from country to country. In the USA, batteries account for 85% of lead production, whilst in the UK, consumption of lead sheet for architectural soundproofing has been promoted and is nearly in the same order as batteries. In Japan, California and other earthquake-prone areas, the value of lead-rubber base isolation systems for critical buildings such as hospitals has been recognised, and growth of lead in this application is expected to be strong [2].

2.3 Lead-acid batteries are the key growth factor

The growth in demand for lead-acid batteries has averaged 3.9% over the last 15 years, or around twice the average rate of demand for all lead [1]. Other uses declined by approximately 500 kt in the same period. Further significant growth in demand is expected for lead in batteries, due to growth in vehicle fleets and usage (especially in emerging and transitional economies), electric and hybrid vehicles, and back-up power systems for electronic equipment and remote independent power supply systems.

As a consequence of the increasing requirement for batteries, the demand for lead is expected to increase at a faster rate in the first part of the 21st century than it has in the latter half of the 20th century, assuming the same average economic conditions.

2.4 Increased recycling of spent batteries

The tighter legislation surrounding lead use that has resulted in this change in consumption pattern, has also caused an increase in the proportion of lead products recycled. The increase in recycling has been facilitated by improved collection and handling systems in most countries.

The properties of lead in batteries also gives it an unusually short life cycle relative to other metals and applications. Research by the Battery Council International in 1995 indicated quite variable life spans of automobile batteries in different countries, with a range from two to five years. Other lead products have considerably longer life spans before re-appearing, if ever, for secondary processing.

The costs of production from recycled secondary materials are also lower than from primary materials (concentrates from mined ores). Less energy is consumed and less slag and secondary emissions such as sulphur are produced.

The combined result of these factors is growth in the proportion of secondary materials used in the world's lead production from 44% in 1985 to 61% in 1999 [1]. In the USA secondary materials may now account for 85% of the total lead production [3].

3 Production of lead from secondary materials

3.1 Smelters need flexibility

Primary smelters that use conventional sinter plant and blast furnace/ISF technology can usually handle no more than 5% of secondary materials in their feed. This limitation reduces the operating competitiveness of these smelters as the availability of secondary materials and the attractions in processing them (such as reduced slag make) increase.

New bath smelting technologies are available which are capable of processing various feed types, including shredded batteries. Ausmelt Technology has been adapted to processing a range of lead bearing materials from concentrates through to shredded secondaries, and is currently being employed for processing secondary lead materials by Metaleurop Weser Blei at Nordenham, Germany and by Korea Zinc at Onsan, Korea.

3.2 The composition of spent lead-acid batteries

When processing primary materials, knowledge of the feed assay is vitally important for efficient, environmentally responsible and profitable operation. This is even more critical in secondary lead processing, where materials are often classsified as scrap or waste and collected and aggregated prior to processing.

The composition of secondary feed material is also likely to vary over the life of a smelting operation. Composition may depend upon the materials used in construction of current products and the evolution of product designs. The variation of the feedstock and the need for flexible operation are important considerations when evaluating or designing a suitable recycling system. A typical lead-acid battery composition is shown in Table 2 [5].

Table 2: Components of a new lead-acid battery

Item	Weight %	Casing Material	
	Component	Ebonite	Polypropylene
1	Active mass (paste)	31.2	35.7
2	Acid (32% H_2SO_4)	25.0	28.6
3	Grids (5% Sb)	19.5	22.3
4	Connectors & posts	5.2	5.9
5	Separators (PVC)	2.2	2.5
6	Casing	16.9	5.0
Total		100.0	100.0

Ebonite (hard rubber) casings were used in 70% of batteries made in 1989. This material has largely been superseded by the much lighter polypropylene (PP), which accounted for 70% of casings by 1994. The average composition, in aggregate, of a new 16 kg polypropylene-cased battery is as shown in Table 3.

Table 3: Composition of a polypropylene-cased battery

Weight	Weight in components (kg)						
Kg	Pb	Sb	H_2SO_4	H_2O	SO_4, Total	PVC	PP
16.0	9.6	0.25	1.5	3.1	1.4	0.4	0.8
Wt%	60	1.6	9	19	8.9	2.5	5

In addition to the fluctuation in sulphate content, alloying elements associated with the grid material also add to the variability of the feed stock. Battery grids are made up predominantly of antimonial lead but may also contain arsenic, tin, copper, telerium and calcium, which will also contaminate the paste.

3.3 Conventional secondary processing

The majority of conventional secondary processing plants utilise a series of breaking and shredding steps before smelting in a reverberatory furnace followed by a blast furnace. Some newer plants incorporate a step of soda leaching the paste prior to smelting in order to eliminate the bulk of the sulphur, thereby greatly decreasing the amount of sulphur to be removed from the process gas. The electric furnace has also been employed in place of the blast furnace.

Conventional secondary lead processing can be summarised into the following stages:

- battery breaking – sulphuric acid is drained and recycled or neutralised, the components (metallics, rubber and separators, M/R/S) are gravity separated for drying and subsequent processing, and polypropylene from the casing is recovered for sale as secondary material,
- leaching of battery paste with soda ash – lead sulphate is converted to lead carbonate and sodium sulphate is recovered for sale to pulp and paper or other industries,
- drying of leached paste and M/R/S components to improve the capacity of the smelting furnace,
- reverberatory furnace – the lead-bearing components are selectively reduced to produce soft lead for refining. Gas is filtered for dust removal in a baghouse then scrubbed to remove residual sulphur,
- blast furnace or electric furnace – slag from the reverberatory furnace is further reduced to produce hard lead bullion and a slag suitable to be discarded.
- as an alternative to the reverberatory furnace - blast furnace combination, two rotary furnaces in parallel are used to reducing smelt the paste to soft lead and to melt the grids to hard lead.

3.4 Evaluation of environmental performance

The traditional practice of recycling lead-acid batteries has associated with it the potential for high levels of lead, acid, sulphur, chlorides and organic pollutants. Making the recyclers' task even more difficult, has been battery manufacturers' push to increase the service life and reduce maintenance of their products. This has resulted in increased complexity of battery design and hence composition. The recycling industry has responded to this pressure with increased attention to improving its processing practices, either by upgrading existing technology or through complete technology/process flowsheet replacement.

The environmental performance of several process routes for recycling lead-acid batteries in commercial use around the world have been described and assessed [5]. These include the methods described above. One of the methods reviewed merely drains the batteries and smelts them in a blast furnace. The other routes are various combinations of the following pre-treatment options:

- separation of the battery components after breaking,
- desulphurisation of paste,
- combined or separate smelting of grids and paste.

There are also three basic smelting options following pre-treatment:

- smelting in a reverberatory furnace followed by slag reduction in a blast furnace,
- grids melted and paste reduced in separate rotary furnaces, or
- two stage bath smelting using Ausmelt Top Submerged Lance (TSL) technology.

Several of these processes have now become technically obsolete, economically unattractive or environmentally unacceptable over the last two decades with the implementation of new environmental regulations and the arrival of new technologies for spent battery processing. Among the reasons for obsolescence are inability to meet the regulations for safe disposal of slags, and emission of dioxins and furans (which arise from the breakdown of PVC components).

Best available technology includes steps for automated battery breaking and component separation and smelting by a process which eliminates sulphur and fixes it in an environmentally acceptable way and which produces a non-hazardous, disposable slag, ie a fayalite rather than a soda or soda-matte slag. Also required are modern gas extraction systems for protection of workers' health in such environments, and control of gaseous and aqueous emissions to acceptable standards.

4 Ausmelt Technology for Secondary Lead Processing

4.1 A Review of Ausmelt Technology

Ausmelt Technology is a versatile, low cost, high intensity furnace system for smelting ores and concentrates and for recovering valuable materials from waste or discarded materials. Benefits are usually observed in profitability, environmental performance, operations and maintenance compared to traditional or competing technologies.

It has been applied commercially for various metal and material types including tin, zinc, copper and lead production. By early 2001 there were sixteen commercial scale Ausmelt plants constructed and operable around the world, with seven more in design and construction. The technology has been extended further to include successful demonstration scale plants for pig iron production and treatment of spent pot lining from aluminium smelting.

The superior process flexibility of the Ausmelt system emanates from the ability to accept varying feed types, operate at different but precisely controlled oxygen potential, and recover heat from post-combustion reactions to the bath. The system effectively separates volatile species to fume, valuable non-volatile species to metal and low-value non-volatiles to a stable, discardable slag.

The superior environmental performance derives essentially from the totally enclosed furnace operating under negative pressure and the sealing of all ports via specially designed devices. When processing secondary lead materials the post-combustion of process gases at temperatures in excess of 1300°C followed by rapid cooling results in levels of dioxins and furans well below statutory levels (< 0.1 ng/m^3 TEQ). These unique features are particularly well suited to the requirements of the secondary lead smelting industry.

A brief comparison of the advantages of Ausmelt Technology when compared with existing technologies such as the blast furnace, the reverberatory/ blast furnace combination and rotary furnaces is presented in Table 4.

Table 4: Ausmelt Technology versus the blast furnace, the reverberatory / blast furnace combination and rotary furnace

	Blast Furnace	Reverb/Blast Furnace	Short Rotary Furnace/ Rotary Kiln	Ausmelt Furnace
Production of stable, fayalite slag	Yes	Yes	No	Yes
Control of fugitive emissions	Difficult	Difficult	Difficult	Simple Well sealed furnace with responsive pressure control
Control of dioxin and furan emissions	Post combustion by external device	Post combustion by external device	Post combustion by external device	Dioxin & furan formation avoided by lance post combustion and rapid cooling
Sulphur Fixation:				
- undesulphurised paste	Iron-lead matte	SO_2 scrubber	Soda matte	SO_2 scrubber
- desulphurised paste	---	Disposal of Na_2SO_4	Disposal of Na_2SO_4	Disposal of Na_2SO_4
Quantity of slag:				
- undesulphurised paste	High slag make	Low slag make	High slag make (soda matte)	Low slag make
- desulphurised paste	---	Low slag make	Low slag make (soda slag)	Low slag make

4.2 Ausmelt Process Flowsheet

Treatment of secondary lead materials using Ausmelt Technology is a two stage process requiring a smelt stage followed by slag reduction. Figure 1 describes each of the process stages. Each stage revolves around a series of oxidation and reduction reactions in which lead sulphide, sulphate and oxide are reduced to lead metal. The predominating lead reactions in both stages are described below.

Smelt (Stage 1):

$PbS + 1.5O_2 = PbO + SO_2$ $\qquad$ $PbS + O_2 = Pb + SO_2$

$PbSO_4 = PbO + SO_2 + \frac{1}{2}O_2$ $\qquad$ $PbO + C = Pb + CO$

Slag Reduction (Stage 2):

$PbO + C = Pb + CO$

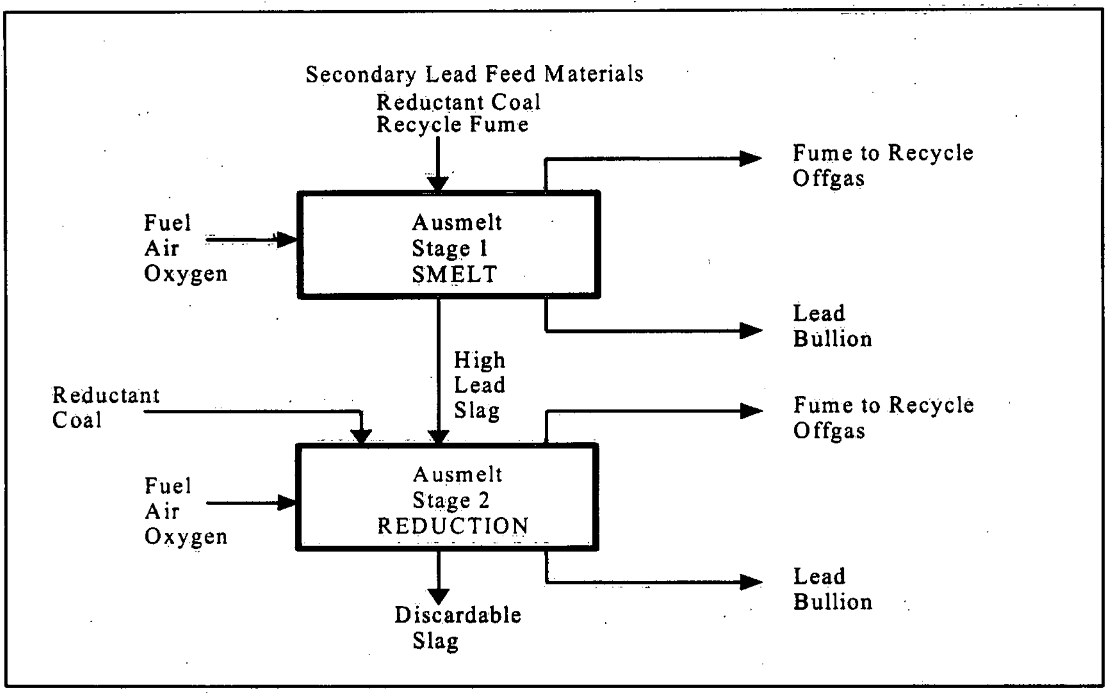

Figure 1: Schematic flowsheet – two stage process for secondary lead materials

In both stages afterburn air is introduced into the top space of the furnace(s) through a shroud pipe attachment on the Ausmelt lance to post-combust any volatilised species including, lead, lead sulphide , and any uncombusted coal products such as carbon monoxide, hydrogen and volatiles. Up to 40% of the energy generated by these reactions is recovered to the bath by the splashing slag. This recovered energy helps to offset the primary energy requirement supplied by submerged combustion of fuel.

The two stage operation can be carried out in a single or dual furnace arrangement depending on the scale of the operation. For single furnace operations the smelt and reduction stages are carried out in succession. In a dual furnace arrangement, the smelt operation is carried in the first furnace, with slag flowing continuously into the second furnace where lead contained in slag is reduced, Figure 2.

During the smelt stage secondary lead materials, fluxes and reductant coal are fed to the furnace at operating temperatures of 1000 to 1100°C. Depending on the sulphide to sulphate, and metallic lead content of the feed, the furnace is operated under reducing, neutral or oxidising conditions by adjusting the ratio of feed to reductant coal and/or the proportion of fuel to combustion oxygen.

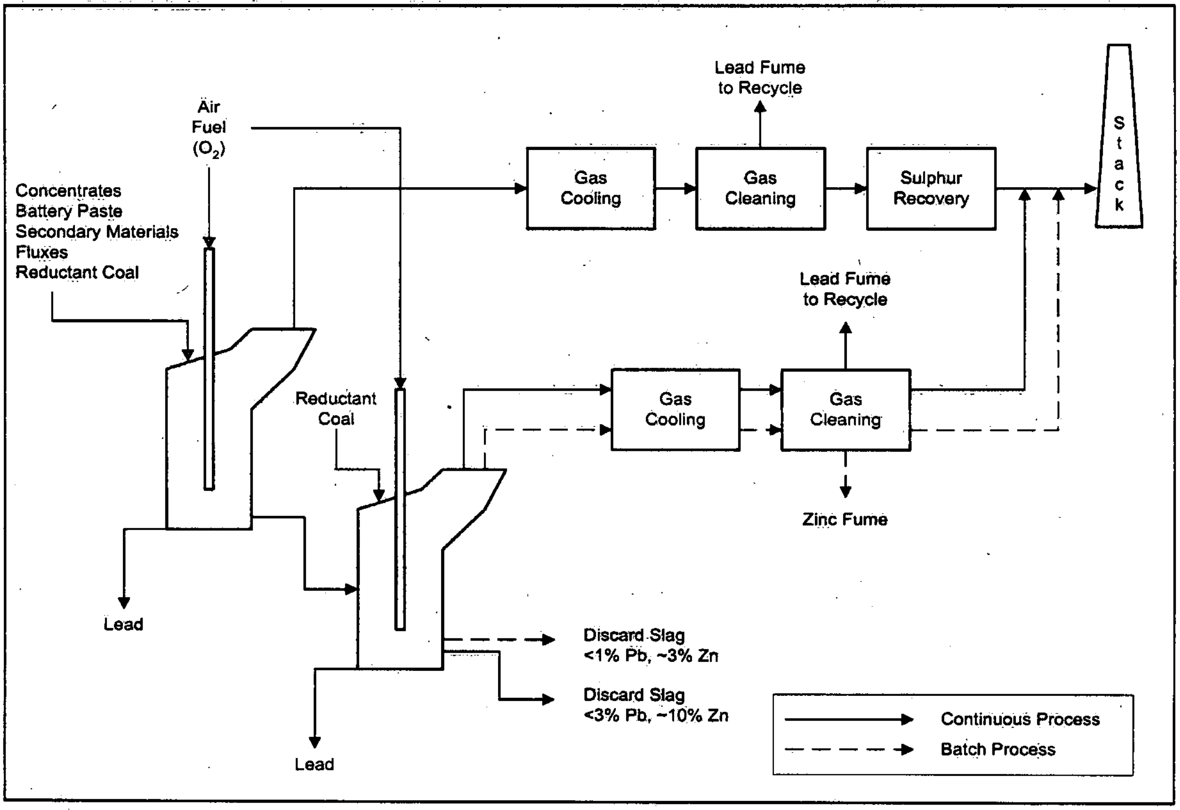

Figure 2: Two Furnace Continuous Process or Two Furnace Continuous/Batch

Lead bullion, fume and a high lead slag are produced. In the two furnace arrnagement lead bullion and slag are removed continuously. The slag is transferred to the slag reduction furnace, as depicted in Figure 2. For the single furnace arrangement once the furnace capacity has been reached feeding is stopped and the slag reduction stage commences. The lead bullion can be removed continuously whilst smelting or at batch intervals depending on the nature of the bullion handling system.

The lead content of the slag is determined by the grade of materials smelted, but is typically of the order of 40 to 50% for processes smelting battery secondaries.

During the slag reduction stage, reductant coal is fed to the bath to maintain a low oxygen potential in the order of 10^{-9} to 10^{-10} atmospheres. The lead oxide in slag is reduced to produce bullion, lead bearing fume and slag containing less than 3% lead. The furnace temperature during this stage is raised to 1250°C to maintain a liquid slag as the lead content in slag decreases. A second, short reduction step can be carried after the removal of bullion to decrease the lead content in slag to less than 1%. In the case of the two-furnace system, the inclusion of this second small reduction stage requires that the slag from the smelting furnace be transferred periodically to the slag reduction furnace.

The flexibility of Ausmelt Technology enables various flowsheets to be developed depending on the secondary material type, the material pre-treatment stages involved and the desired lead levels in the final slag. The Technology has the ability to process whole drained batteries including the plastic casings, a combination of battery undesulphurised paste and grids and desulphurised battery paste and grids. Figures 3, 4 and 5 are flowsheets for each of the three options.

4.3 Treatment of whole drained / shredded batteries

For the case of whole drained batteries (Figure 3) the shredded plastic components, grids and paste are typically processed to produce soft lead (~0.1% Sb) from the smelt stage and hard lead (~20% Sb) from the reduction stage. The plastics associated with the battery casings and separators volatilise on contact with the bath and the resulting gaseous hydrocarbons are post-combusted in the top space above the bath. The high exhaust gas temperatures (> 1300°C) achieved in the top section of the furnace ensure complete breakdown of any chlorinated organics. Rapid cooling of these gases upon exit of the furnace prevents the formation of dioxins and furans.

The gases from both stages are cooled and filtered using conventional process gas equipment. Gases from the smelt stage are treated in an acid plant or scrubbing system to capture the contained sulphur dioxide. The dusts recovered from the process will contain chlorinated species from the decomposition of plastic components such as PVC. Before the dust can be recycled to the smelting stage the chlorine contained in the dust must be removed through reaction with a dechlorinating agent such as sodium carbonate.

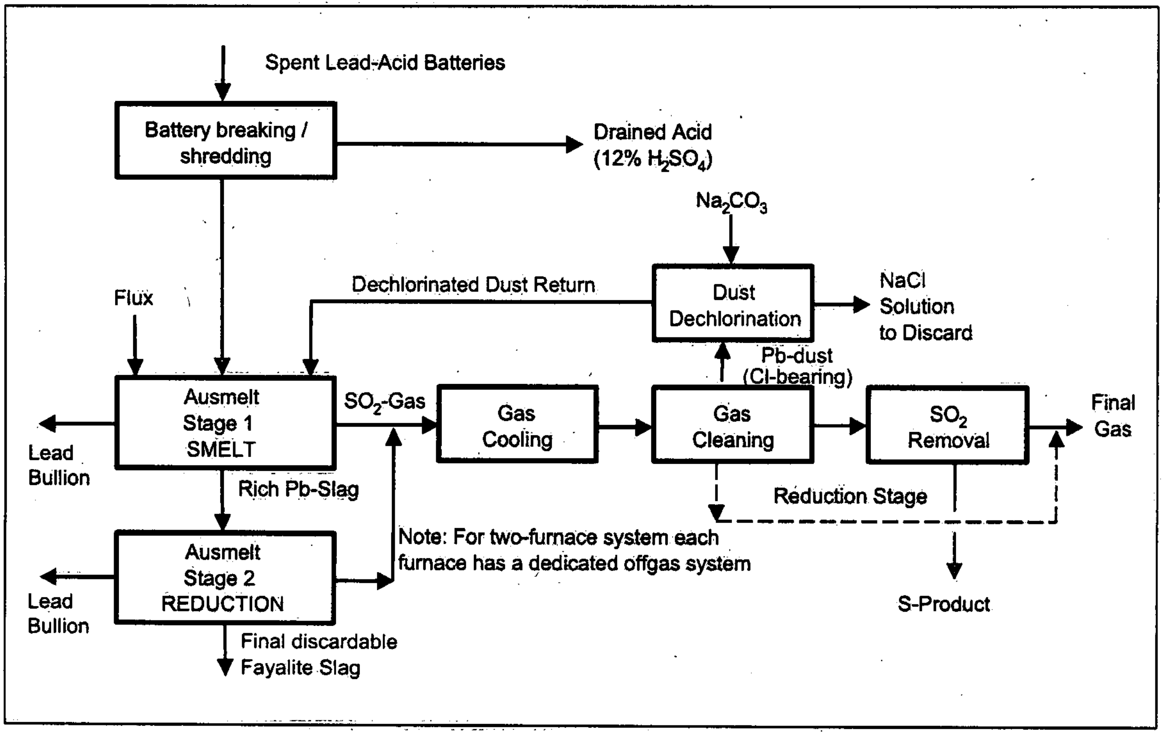

Figure 3: Treatment of whole drained batteries

4.4 Treatment of undesulphurised battery paste and battery grids

The most significant effect of separating the plastics from the battery paste and grids after battery shredding (figure 4), ie processing the battery paste and grids only, is that it

(a) reduces the air requirement for post-combustion in the Ausmelt furnace(s), and

(b) removes the need for dust dechlorination. The smelt and reduction stages are effectively the same as for treatment of whole drained batteries.

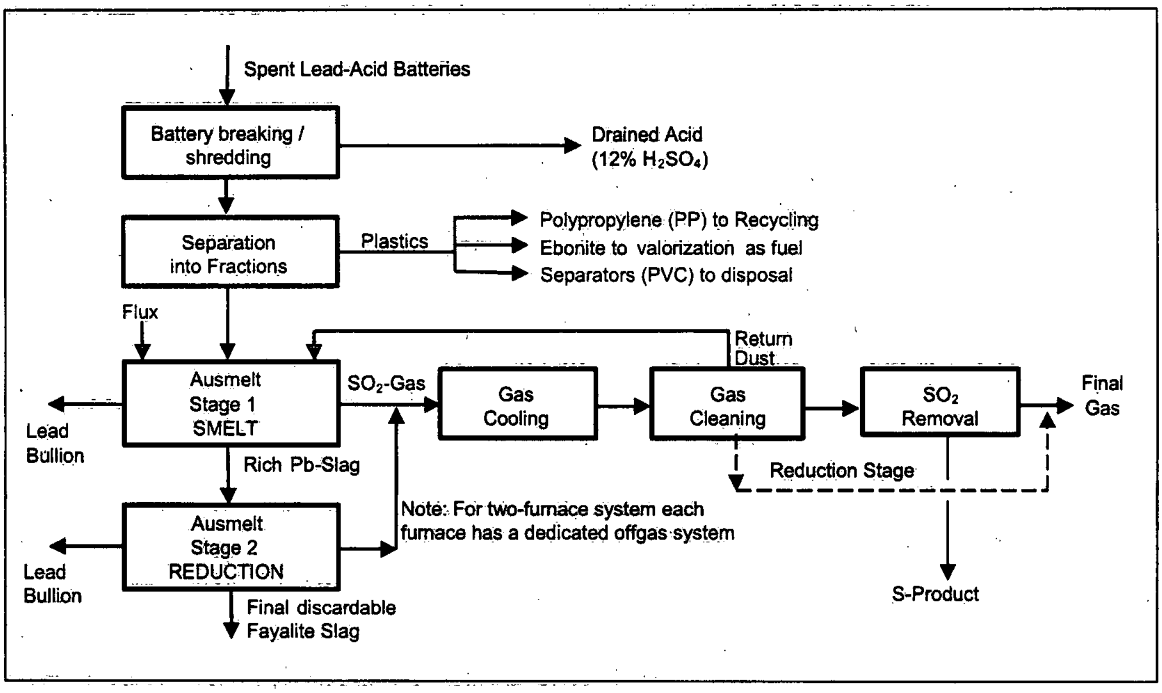

Figure 4: Treatment of undesulphurised battery paste and battery grids

4.5 Treatment of desulphurised battery paste and grids

Desulphurisation of the battery paste (figure 5) and subsequent feeding a mixture of desulphurised paste and grids to the Ausmelt furnace eliminates the need for a complex sulphur fixation system to remove sulphur from the exhaust gases, ie. acid plant. Whether the bulk of the sulphur is best removed and fixed before or during the smelting stage is a matter to be decided in each case.

It should be noted that in all cases of desulphurisation of paste, sulphur removal is not complete. Of the 6 % S in the paste, approximately 80 to 85 % is removed by leaching, leaving 1 % S in the desulphurised paste. This residual sulphur will be eliminated during smelting necessitating a residual SO_2 removal step in the exhaust gas handling system.

Given the requirement to desulphurise gases even from desulphurised paste, it is expected that the treatment of undesulphurised pastes will be more cost competitive because of the lower capital investment in the pre-treatment of the batteries. Of course, selection of the preferred operating approach will be influenced by local and existing infrastructure, and whether the materials are desulphurised will need to be determined on a case by case basis.

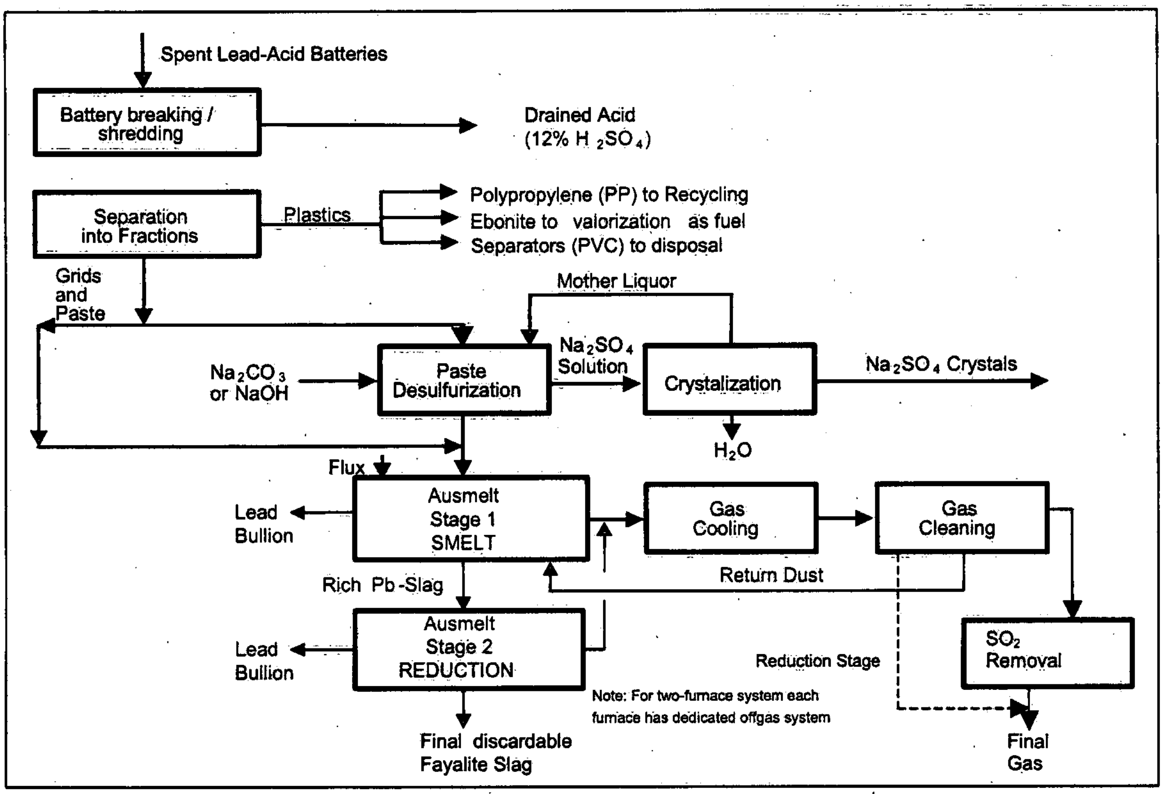

Figure 5: Treatment of desulphurised battery paste and battery grids

5 Turnaround at Metaleurop Nordenham

5.1 Flexibility the Key

Metaleurop Weser Blei retired its traditional process of lead smelting by sinter machine and blast furnace at Nordenham, Germany in 1996 and commissioned a system based on Ausmelt Technology. There were economic, environmental and technical reasons for this change.

The new plant now processes several feed materials including secondary scrap, and was expected to reduce the cost per tonne of lead produced by 20%, due to reduced inputs of energy, personnel, services and maintenance [7].

The extreme versatility of the new smelter enables it to handle a feedstock of up to 100% scrap and lead residues, while the sintering blast furnace could only take a maximum of 5% with the remainder being concentrate. This allows Metaleurop to respond quickly to changing market conditions for scrap and concentrates.

5.2 Improved Environmental Performance

Replacement of the sinter machine and blast furnace with Ausmelt Technology together with other equipment changes at Nordenham has lead to strong improvements in environmental performance. All emissions have been drastically reduced, for example Pb, Cd, Sb, As, Tl, Hg, SO_2 reduced by between 94 and 99.3%.

Energy consumption per tonne of lead has been reduced by 35%, and emission of CO_2 per tonne reduced by 59%. This was partly due to the ability of the new system to allow conversion from coal to natural gas as fuel, and partly due to greater fuel efficiency.

Water consumption decreased by 3 million m^3/y because of the new cooling system of furnace and better energy efficiency. Less primary slag is produced by processing more treated battery paste and less concentrates. Separate campaigns for slag cleaning and zinc fuming to low metal levels in the slag are run on the same furnace from stockpiled high-lead slag produced from high grade feeds when bullion is being produced [8].

6 Conclusions

A clear trend in lead processing is that for increased recycling. The rate of growth in processing of secondary lead materials is approximately twice the rate of growth in lead production overall.

The lead acid battery has become the dominant end-use product for lead. Demand for this type of battery is increasing in most regions of the world, and there is no alternative or competing product in the short- or medium-term future. Batteries are also very suitable for recycling in terms of both their physical properties and the existence of social systems such as legislation and collection channels in most countries.

Ausmelt Technology is well suited to processing secondary lead materials, including batteries. This is because of the technology's flexibility in being able to handle batteries in whatever form, including whole drained batteries or the component parts. It can also handle lead concentrates, and thus is able to exploit local and temporary market niches.

The technology is also attractive for retrofitting in existing processing facilities because of its relative low cost, simplicity and small footprint. For the same reasons it would be attractive where opportunities might exist for greenfield lead processing facilities.

Ausmelt Technology has benefits in terms of compliance with the increasingly stringent environment protection regulations relating to lead processing in most countries. This is due to the fundamental design features of Ausmelt furnace systems which give superior performance in controlling emissions and producing discardable slags. Finally, Ausmelt Technology is now commercially proven in large scale operations in Europe and Asia.

7 References

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